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We report surface vibrations in c(2x2) oxygen adlayers on Ni and Co thin films on a Cu(001) substrate measured at Γ by high resolution EELS. For the Ni thin film surface, one phonon peak is measured for varying film thicknesses from 1.3 ML (monolayer) to 6 ML with a constant energy of ~221cm^{-1}. For the Co thin film surface, three loss peaks are found, whose relative intensities change as the film thicknesses are varied. One loss peak ca. 520cm^{-1} is tentatively assigned to the Fuchs-Kliewer mode of cobalt oxide (CoO). The other two peaks at 317cm^{-1} and 376cm^{-1} are likely related to different bonding sites. Surface phonons on the p(2x2) Co thin film (389cm^{-1}) and a bulk resonance mode (115cm^{-1}) are also reported.

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Vibrational Spectroscopy of Ordered Oxygen Adlayers on Ni/Cu(001) and Co/Cu(001) Thin Film Systems

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We report surface vibrations in c(2x2) oxygen adlayers on Ni and Co thin films on a Cu(001) substrate measured at $\bar{\Gamma}$ by high resolution EELS. For the Ni thin film surface, one phonon peak is measured for varying film thicknesses from 1.3ML(monolayer) to 6ML with a constant energy of ~221cm^{-1}. For the Co thin film surface, three loss peaks are found, whose relative intensities change as the film thicknesses are varied. One loss peak ca. 520cm^{-1} is tentatively assigned to the Fuchs-Kliewer mode of cobalt oxide (CoO). The other two peaks at 317cm^{-1} and 376cm^{-1} are likely related to different bonding sites. Surface phonons on the p(2x2) Co thin film (389cm^{-1}) and a bulk resonance mode (115cm^{-1}) are also reported.

Introduction

Epitaxial thin films usually have different lattice structures from their bulk structures, and as a result, their electronic, magnetic , elastic and chemical properties are expected to be quite different from the bulk states [1]. Early and current interest in thin films for catalytic use is suggested through application of the metastable chemical properties [2]. Recently, the magnetic properties of ultrathin films of ferromagnetic bulk material on paramagnetic substrates and the predictions of magnetic dead layers have induced strong interest in experimental and theoretical research[3]. The work to date needs structural information of thin films as an essential part, because the magnetic moments of thin films are expected to depend on the atomic volumes of the thin films[4]. Recently clean thin film surfaces of Ni[5] and Co[6] on a Cu(001) substrate were studied by HREELS (High Resolution Electron Energy Loss Spectroscopy) in order to probe their geometric and vibronic structure by the current authors. Present work reported here for surface phonons of oxygen adlayers on the epitaxial thin films were directed towards the chemical properties of the epitaxial films, e.g. the bonding properties and the vibrational properties of ordered light atoms on the thin film. Oxygen is chosen because of its chemical importance. Further, it is one of the most studied adlayer systems on bulk Ni(001)[7] and bulk Cu(001)[8], so we can directly compare its properties on the thin film surface with those on both bulk surfaces. These works combined with former works on structural and elastic properties on thin film surfaces[5][6] are expected to contribute to the systematic understanding of thin films.

5 minutes, the LEED pattern sharpened and exhibited very low diffusive background. Auger spectra remained as before annealing the sample. In the following discussion, this sample preparation procedure is referred to as the "standard procedure".

Clean Ni thin films did not show any interdiffusion of Ni and Cu even after annealing to ~490K[5]. For Co thin films without adsorbed oxygen, even annealing the sample at lower temperatures (~440K) caused interdiffusion of Co and Cu, judged from the simultaneous increase of Cu AES peaks and decrease of Co AES peaks. A recent comprehensive study on Co thin film growth on a Cu(001) substrate showed similar behavior[10]. This interdiffusion is confirmed by experiments summarized in Fig. 1. We measured phonon spectra with HREELS in the specular position on three differently prepared surfaces: Spectrum A is the surface phonon data on the sample surface prepared by the standard procedure. Spectrum B is the phonon spectrum on the surface where the same amount of oxygen is dosed on a pre-annealed Co film. We found a dim and blurred but clearly discernable c(2x2) LEED pattern on this surface. Finally, Spectrum C is the phonon spectrum where the same amount of oxygen is dosed on the clean Cu substrate. For this case no fractional-order LEED spots were detected. We notice the similarity of spectra B and C and the quite distinct character of spectrum A. This is consistent with the interpretation of the Auger spectrum change as due to the interdiffusion of Co and Cu on the clean Co thin film, and the stability of the Co thin film prepared with an oxygen adlayer. A broad shoulder in the high energy side of the B spectrum is believed to arise from remnant Co on the Cu substrate surface. The surface free energy of the thin film is thought to be lowered by the chemisorption of oxygen, making the Co thin film more stable. The stability of O/Co/Cu(001)

system is also confirmed by comparison of the phonon data before and after annealing the c(2X2) adlayer system prepared on the un-annealed Co thin film as shown in Fig. 2. From the figure we can see no qualitative change in the spectrum occurs in traces A and B. Annealing has only improved the order of the surface, resulting in the resolution of two peaks from the one broad peak. This shows the possible usage of oxygen as a segregating surfactant[11] (surface active species) which stabilizes the overlayer by lowering its surface free energy in heteroepitaxial growth.

Results and Discussion

a. C(2x2) Oxygen adlayer on Ni/Cu(001) system

In Fig. 3 are shown very intense loss spectra measured at the zone center $\bar{\Gamma}$ for several different film thicknesses. The mode energy is around 221cm^{-1}. A wide range of incident electron energies was employed to find other modes at $\bar{\Gamma}$ and only null results were obtained. This mode is tentatively assigned to the oxygen vibration normal to the film surface because this mode generates a prominent dipole field in vacuum, as has been shown for the bulk surface[7]. This is consistent with the prediction from the generally accepted position of the oxygen atom, in a hollow site made by four surface Ni atoms for c(2x2) oxygen adlayer on the bulk Ni(001) surface. The local symmetry around the oxygen atom is then C_{4v} and the oxygen modes at $\bar{\Gamma}$ are polarized strictly perpendicular (the A_1 mode) and parallel (the E modes) to the surface. Then from the dipole selection rule[12] only the A_1 mode is observable in specular direction. For the bulk Ni surface the energy of this A_1 mode is 320cm^{-1}[7]. If the above assignment is correct, we are seeing a dramatic softening of this mode by 100cm^{-1}. Assuming the generally accepted position of oxygen in c(2x2) O/bulk Ni, 0.9 Å above the hollow site[7], this softened phonon energy implies ~50 % weakening of oxygen-Ni spring constant from that on the bulk Ni surface[13].

A recent x-ray photoelectron spectroscopy (XPS) study[14] reported that Ni films thicker than 3ML showed similar reactivity as bulk Ni in the formation of Ni oxide on the (001) surface. Abu-Joudeh et al.[15] concluded

that the behavior of the film surface towards oxygen chemisorption is similar to that of bulk Ni from the similarity of EELS [16] (not HREELS) and AES spectra for both the thin film surface and the bulk surface, even for Ni films of around 1ML thickness. Surface phonon studies which work in a lower energy scale (meV range) than XPS, EEL, and AES (eV range), prove to be more sensitive probes for detecting certain differences between the bulk and thin film surfaces.

b. C(2x2) oxygen adlayer on Co/Cu(001) system

In Fig. 4, phonon spectra measured in the specular direction for film thicknesses of 0.7ML, 2ML, 3ML, and more than 6ML are shown. All adlayers are prepared through the standard procedure as described in the former section. Three distinct peaks are found above $300cm^{-1}$ and all are attributed to oxygen-metal vibrational modes, given that their energies are larger than the bulk phonon band edge of bulk Ni which shows a higher Debye temperature than those of both Cu and Co. Their relative intensities change as the film thickness varies. This is strikingly different from the behavior of c(2x2) O/Ni/Cu(001) system, where we find only one peak for thicknesses measured [Fig. 3]. For the thinnest layer, 0.7ML, two peaks with energies $376cm^{-1}$ (type B) and $473cm^{-1}$ (type C) are prominent. For thick films, greater than 6ML, we found one dominant peak with energy $317cm^{-1}$(type A), a small peak with energy $523cm^{-1}$ and a small shoulder reminiscent of type B phonon. For type A and type B phonons, the peak positions did not change, but the type C phonon showed an energy shift as the thickness of the film increased (as shown in Fig. 5), converging to $523cm^{-1}$. For the 2ML film, both limiting film thickness features contribute

giving rise to a broadened peak for type B phonons with appreciable contribution from the type A phonon intensity and a very strong peak of type C. For the 3ML film, the thick film features begin to dominate as shown by a sharp 317cm^{-1} peak with a very small shoulder for the type B phonon.

All three peaks mentioned above show sharp intensity reduction as the measurements depart from the specular direction, as expected for dipole scattering. We measured the phonon spectra for several different incident energies from 2 eV to 40 eV, and no noticeable changes in the relative intensity ratios of peaks were found. Therefore, the spectral changes of Fig. 4 are attributed to intrinsic properties of the sample, not to the artifacts from the method of probing the sample.

From the literature[7], we find that a $q_{||}$= 0 Fuchs-Kliewer mode of bulk cobalt oxide (CoO) appears around 517- 522cm^{-1}, which is near the value of the type C phonon energy of the thick Co film. For a thin oxide film on a metal substrate we are expected to find w_{LO}(longitudinal optical phonon) of bulk cobalt oxide[18] with energy 545cm^{-1}. We tentatively identify the type C phonon as the Fuchs-Kliewer mode of the cobalt oxide film. This interpretation is supported by the recent experimental result from the x-ray search light effect, that Co films up to 2ML include appreciable amounts of clusters[19]. We attribute the large relative intensity of the type C phonon in the thin overlayer (less than 2ML) to be the effect of the enhanced chemical activity of clusters to form oxide. The dramatic drop of the type C intensity for the 3ML film is then an indication of a more planar surface with a reduced number of edge sites associated with cluster imperfections. This interpretation is consistent with the finding of an ideal layer-by-layer growth for 3ML Co films[19]. For thick films, misfit dislocations develop[19,21], offering chemically active sites and

low thickness features, type B and C phonon intensities, grow again. The behavior of the type C phonon frequency with layer thickness [fig. 5] may have its explanation in the dependence of oxide frequency on oxide cluster size. Finally, the increase in the intensity of the type C phonon after annealing the sample can be attributed consistently to the oxidation of cobalt [Fig. 6].

For all thicknesses of the films, we confirmed the c(2x2) oxygen structure with LEED. If oxygen is assumed to occupy the four fold hollow site as is assumed for Ni thin films, we expect only one dipole active vibration at $\bar{\Gamma}$ from the symmetry. The observation of two dipole active modes suggest that oxygen may adsorb at two different sites ,e.g. both bridge sites and four-fold hollow sites, forming two domains of c(2x2) adlayers, which are not distinguishable in the LEED pattern. Then the change of the relative intensity of type A and type B phonon intensities would reflect the relative domain populations as the film thickness varies. Falo et al.[21] studied the CO chemisorption properties on Co thin films of varying thicknesses. They observe the appearance of new peaks in the thermal desorption spectra of CO, which are related to increasingly large number of edge atoms in Co clusters for Co films less than 1ML thickness. This may imply that for films less than 2ML, the number of low coordination number sites (edge sites) associated with clusters are increasing, and they offer a new environment favorable for a new domain for the type B phonon. One other possible answer to the observation of two peaks in specular position is the coexistence of p(2x2) adlayer which is hidden in the LEED pattern. This possibility is excluded because of the finding of a well defined peak on the p(2x2) oxygen adlayer with energy

389cm^{-1} [Fig. 7]. In Fig. 8, we also report the finding of a bulk resonance mode of energy 115cm^{-1}.

Conclusions

In summary, the thin film systems of nickel and cobalt on Cu(001) in the ultrathin regime appear to be quite different. Vibrational data for nickel shows rather ideal growth, in the sense that the oxygen HREELS spectra exhibit a single mode of constant frequency as a function of film thickness. It is interesting to note, however, that this mode is markedly lower in frequency than for bulk nickel.

For cobalt the HREELS spectra are substantially more complex and suggest the presence of clustering at coverages below 2ML as well as oxide formation. By 3ML and higher the films appear to exhibit fewer defects and a lower tendency toward oxide formation. These results, based on a simple, qualitative interpretation of the spectra, demonstrate the ability of HREELS in combination with a probe species (oxygen) to investigate the nature of thin film growth.

Acknowledgements

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Figure Captions

Figure 1.   HREELS spectra from three differently prepared surfaces [A: standard procedure, B: O/ annealed Co/Cu(001), C: O/clean Cu(001)]. The similarity of B and C spectra and the distinct A spectrum confirms the interdiffusion of Co and Cu when annealed without oxygen adlayer and the stabilization of Co layer by the formation of the oxygen adlayer. *:Scale change

Figure 2.   HREELS spectra before and after annealing of Co film with oxygen adlayer. *:Scale change

Figure 3.   Oxygen adlayer phonon for Ni films of varying film thicknesses. In contrast to Co film, they are identical for all films with energy 221cm^{-1} measured at $\bar{\Gamma}$. *:Scale change

Figure 4.   Oxygen adlayer phonons on Co films of varying thicknesses measured at $\bar{\Gamma}$, [I: 0.7ML, II: 2ML, III: 3ML, IV: thicker than 6ML]. *:Scale change
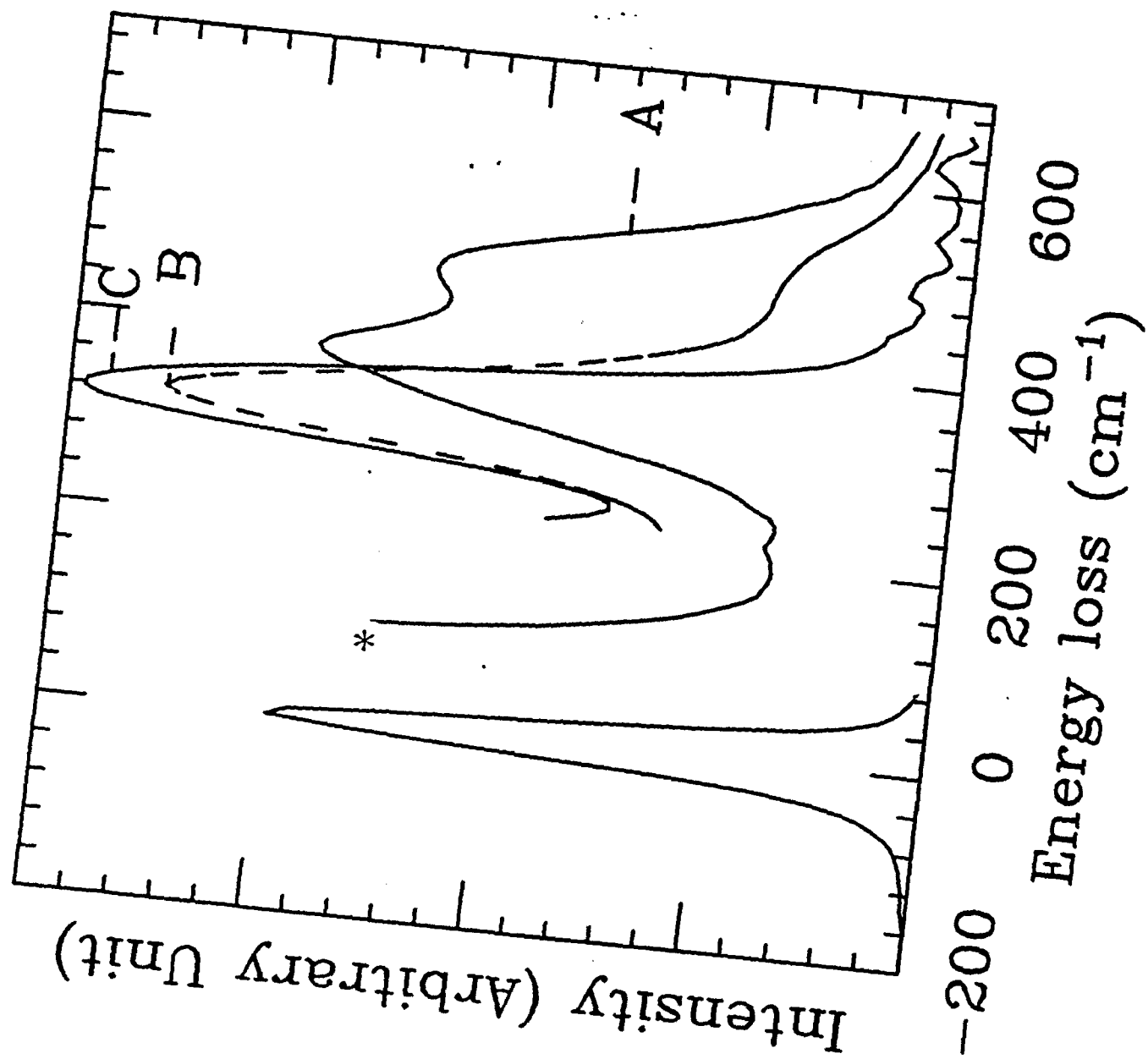
Figure 5.   Energy of type C phonon as a function of film thickness. It converges to a value, 523cm^{-1}, around 3ML thick film.
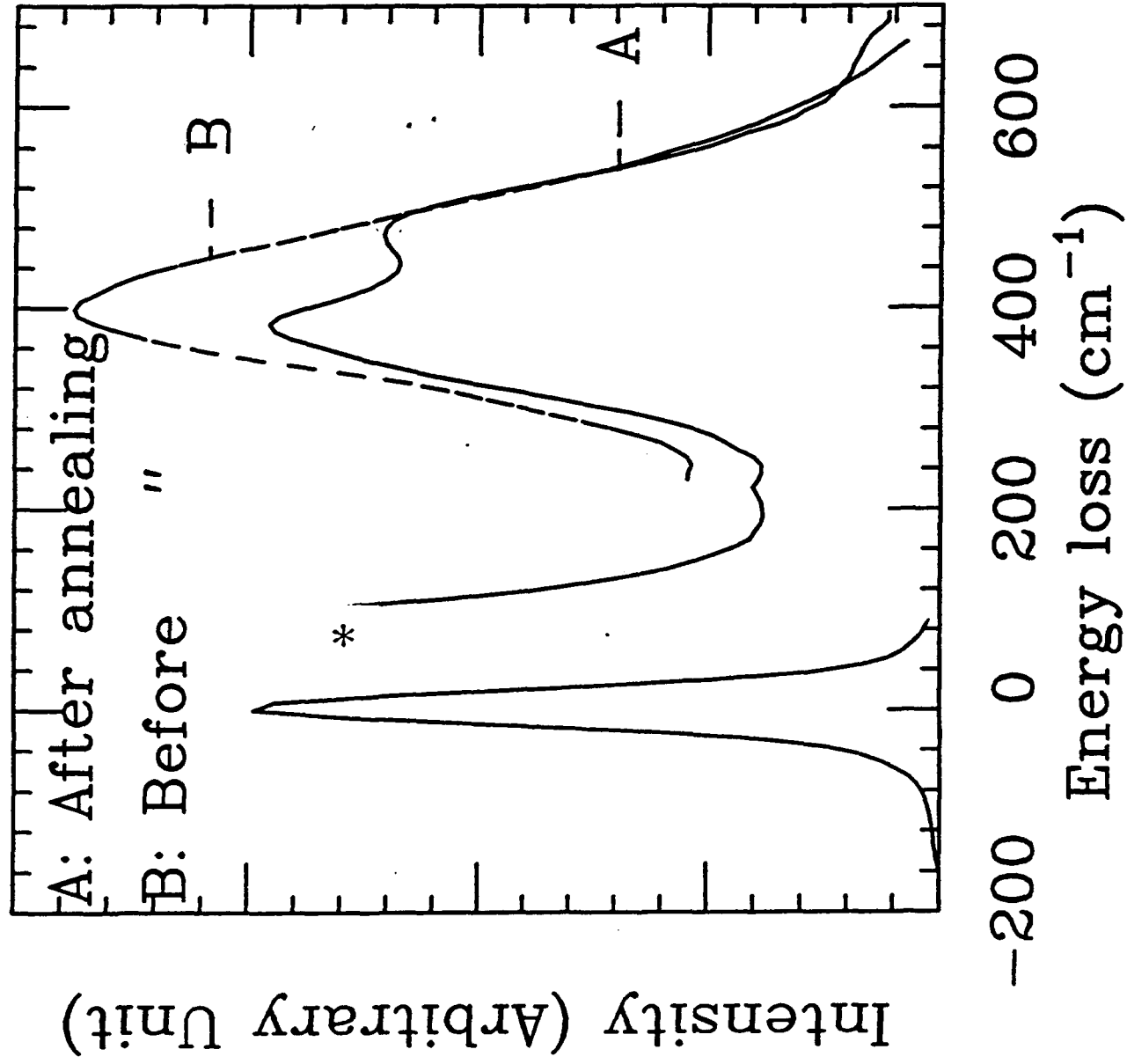
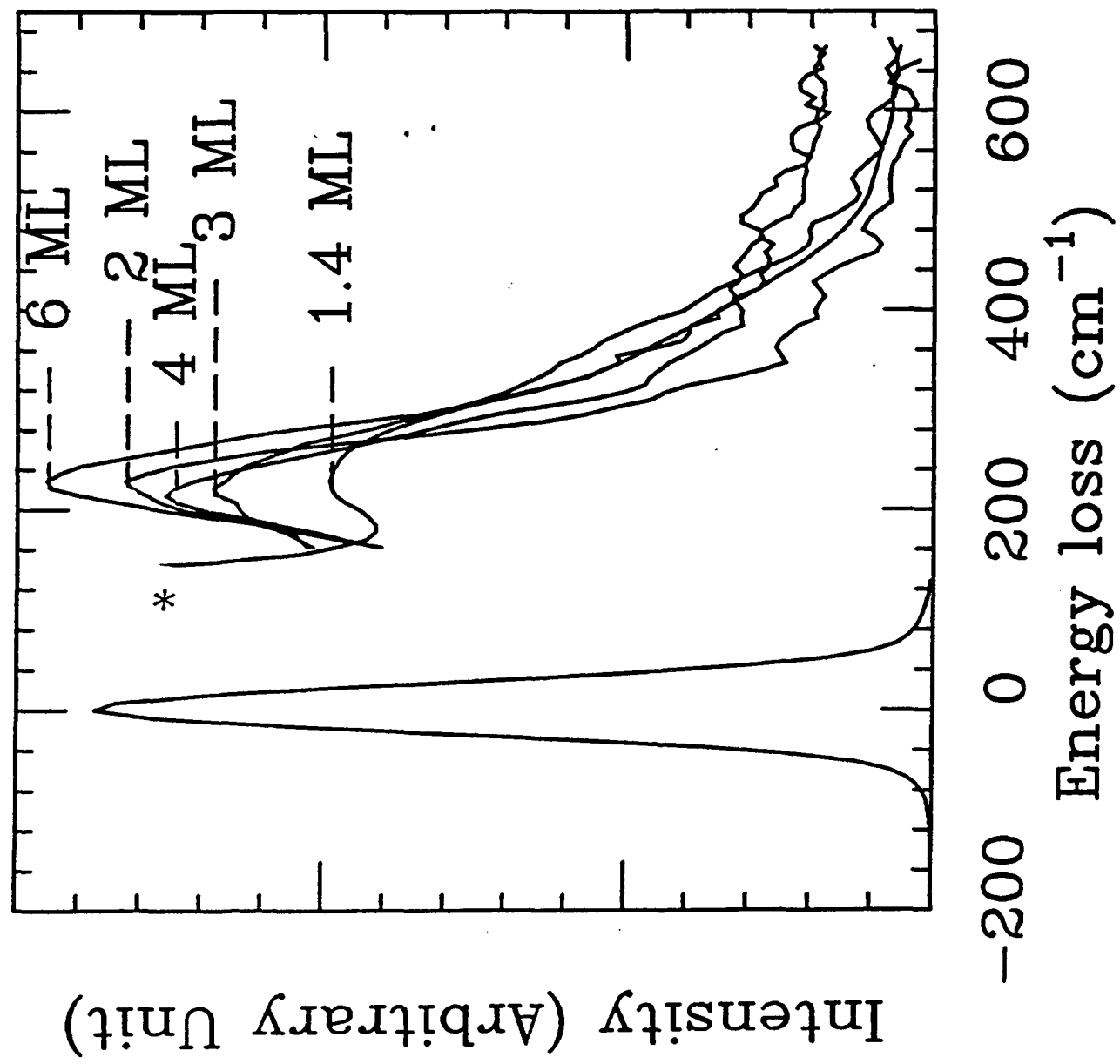Figure 6.   HREELS spectrum of O/(>6ML) Co/ Cu(001) measured at $\bar{\Gamma}$. *:Scale change

Figure 7.   Oxygen adlayer phonon for a p(2x2) oxygen adlayer on thick Co film on Cu(001). Only one well defined peak is found with energy 389cm^{-1}.
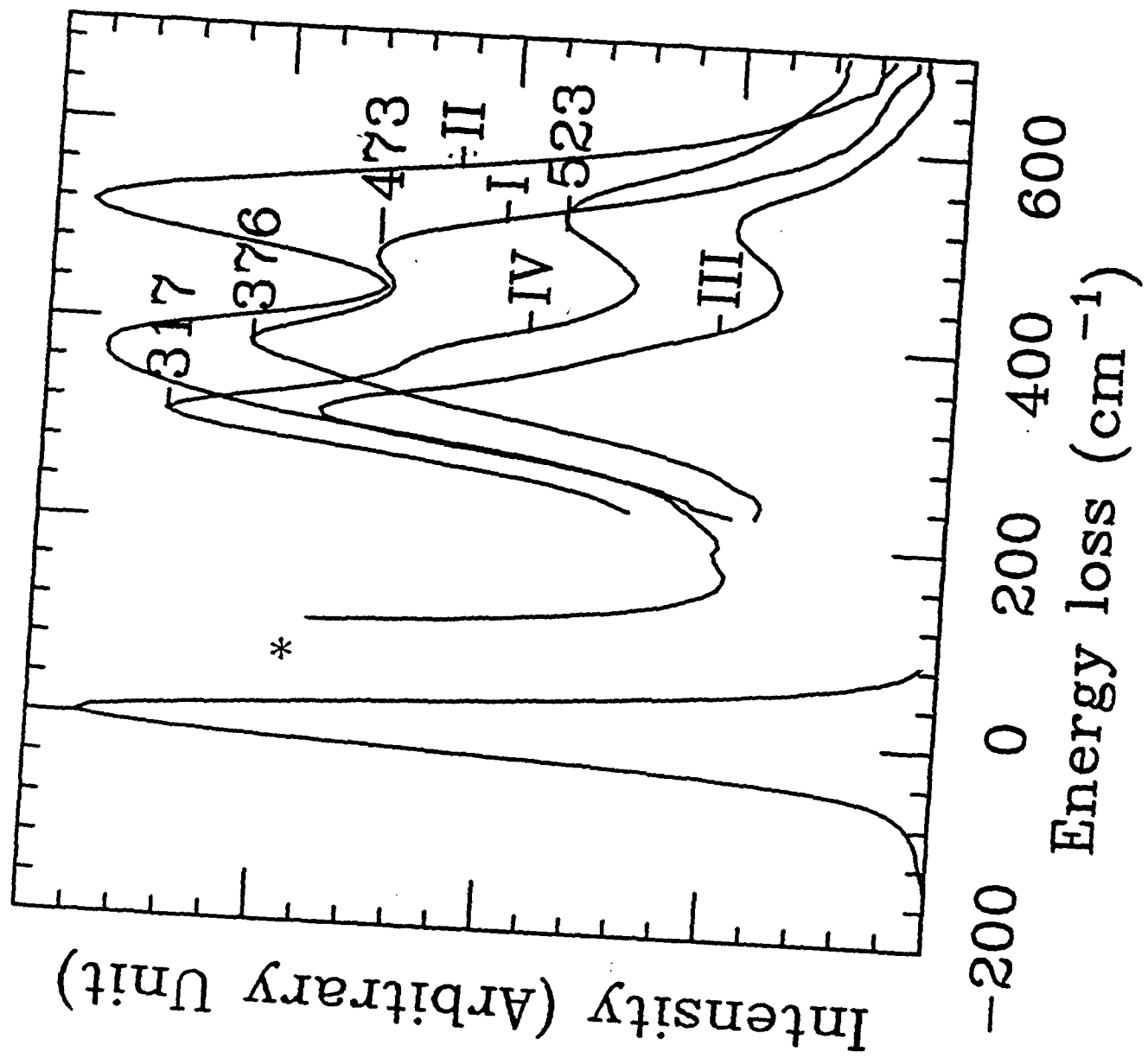
Figure 8.   10° off specular spectrum on c(2x2) O/ 3ML Co/Cu(001) surface. A new peak with energy 115cm^{-1} is found and attributed to bulk resonance
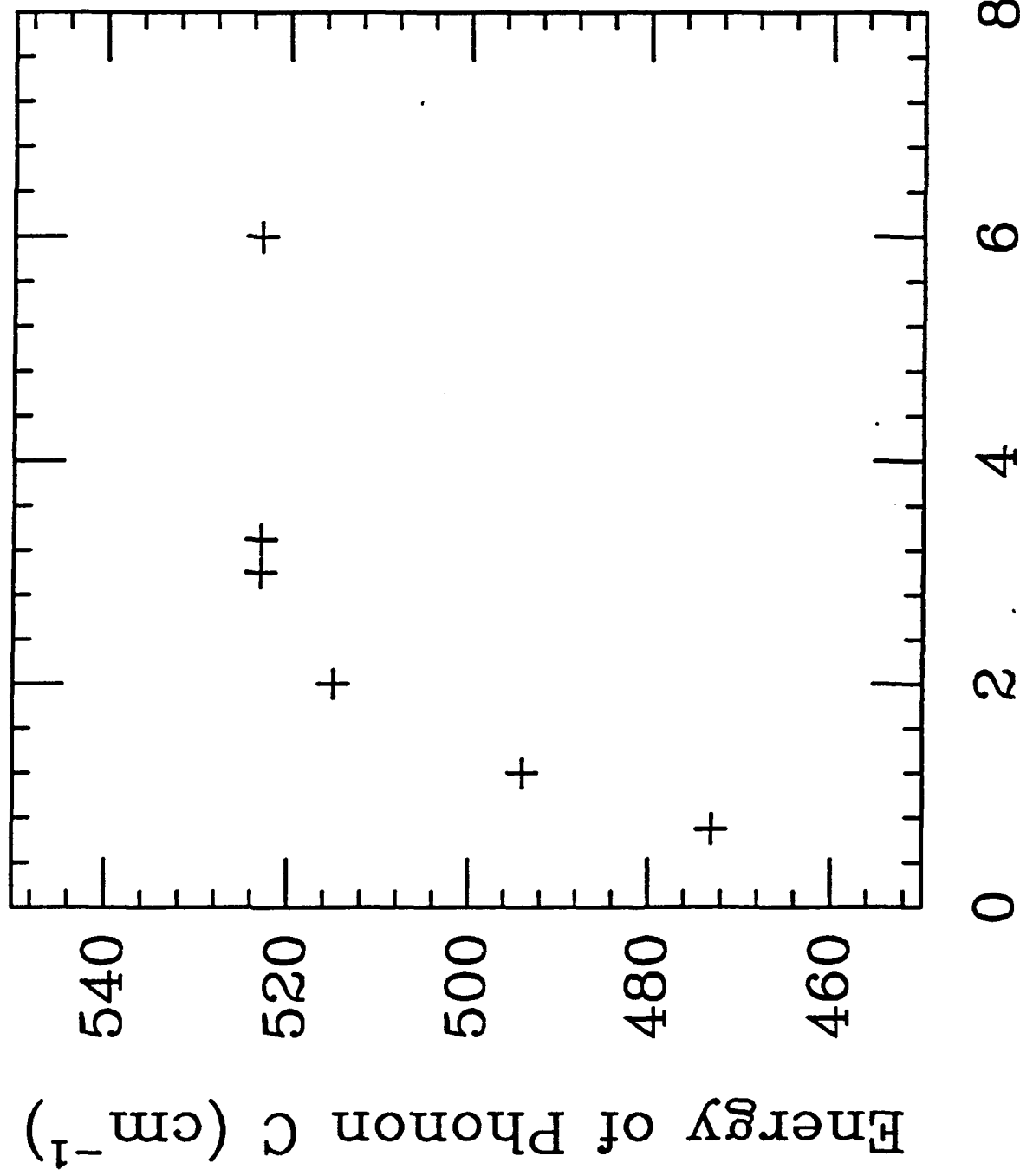
mode. This mode is also observed at the zone center as an unresolved shoulder near the elastic peak.

Intensity (Arbitrary Unit)

Energy loss (cm^{-1})

A

B

C

*

-200   0   200   400   600

A: After annealing
B: Before "

Energy loss (cm^{-1})

Intensity (Arbitrary Unit)

6 ML
2 ML
4 ML
3 ML

1.4 ML

*

Energy loss (cm^{-1})

Intensity (Arbitrary Unit)

-200   0   200   400   600

317
376
473
II
I
523
IV
III
*

Energy loss (cm^{-1})

Intensity (Arbitrary Unit)

-200   0   200   400   600

Energy of Phonon C (cm^{-1}) versus Thickness of Co overlayer (Monolayer)

A: before annealing
B: after

B

A

*

Energy loss (cm^{-1})

Intensity (Arbitrary Unit)

-200   0   200.   400   600

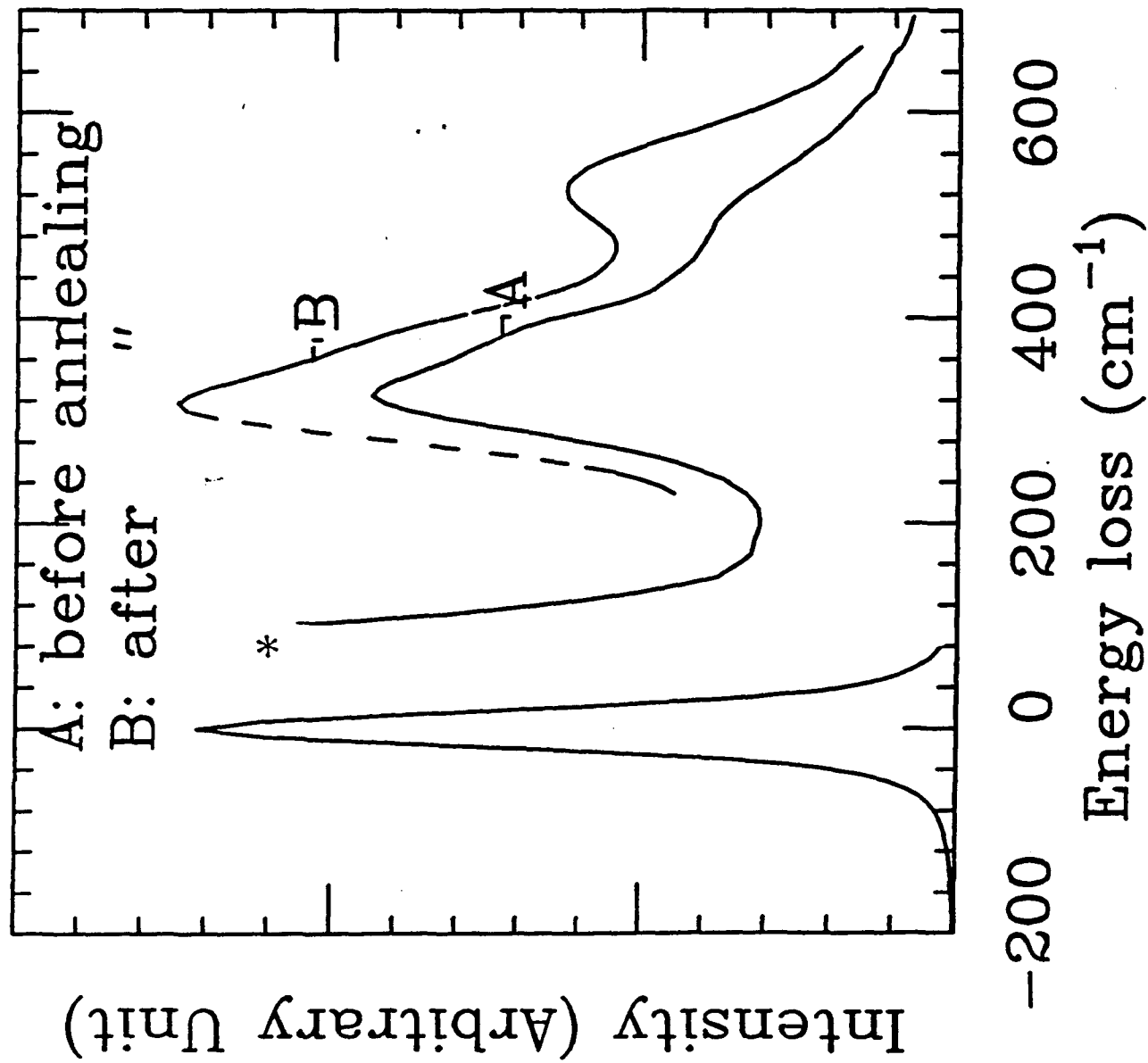P(2×2) O/(>6ML) Co/Cu(001)

389

×500

Energy loss (cm^{-1})

Intensity (Counts per Second)
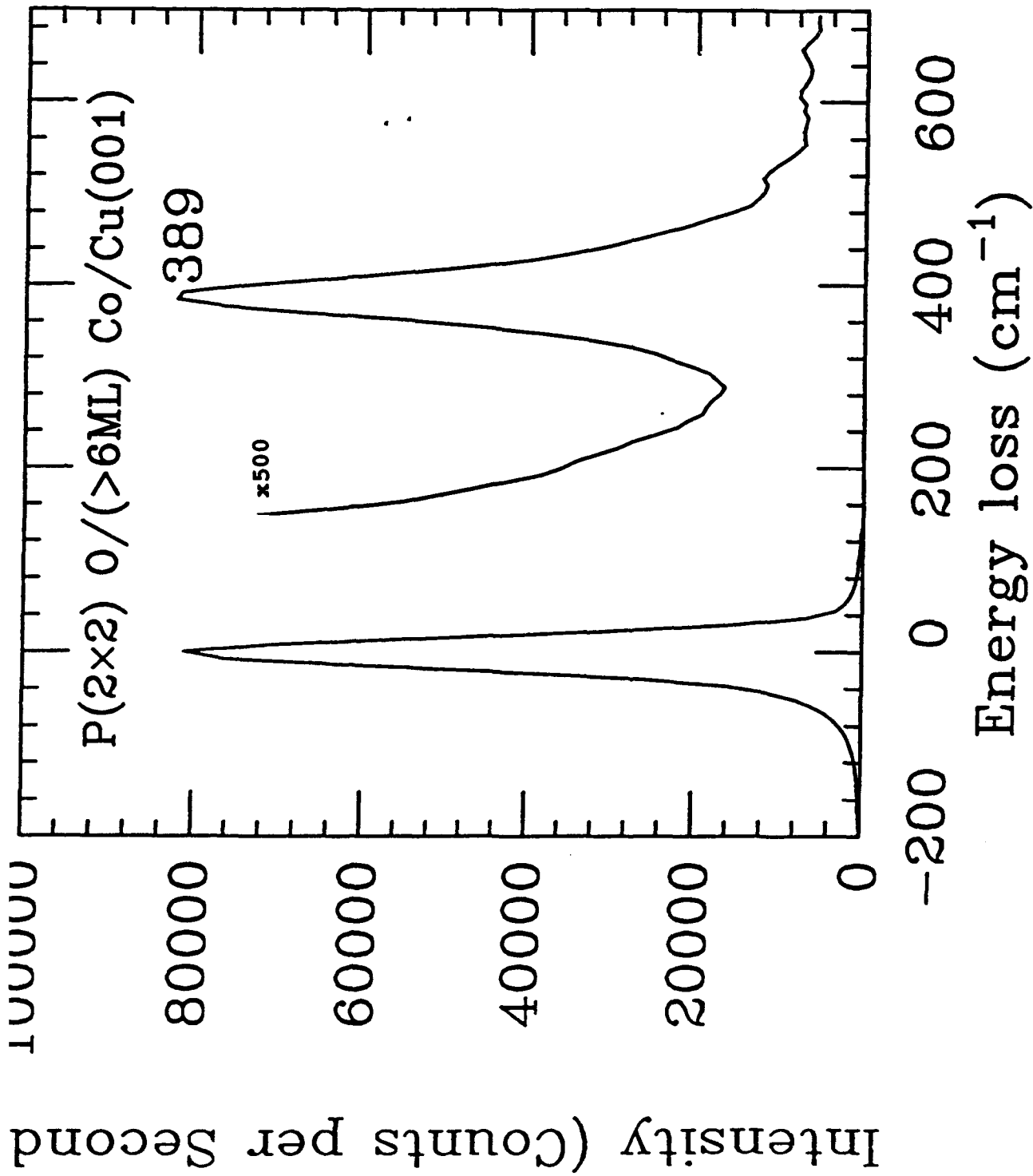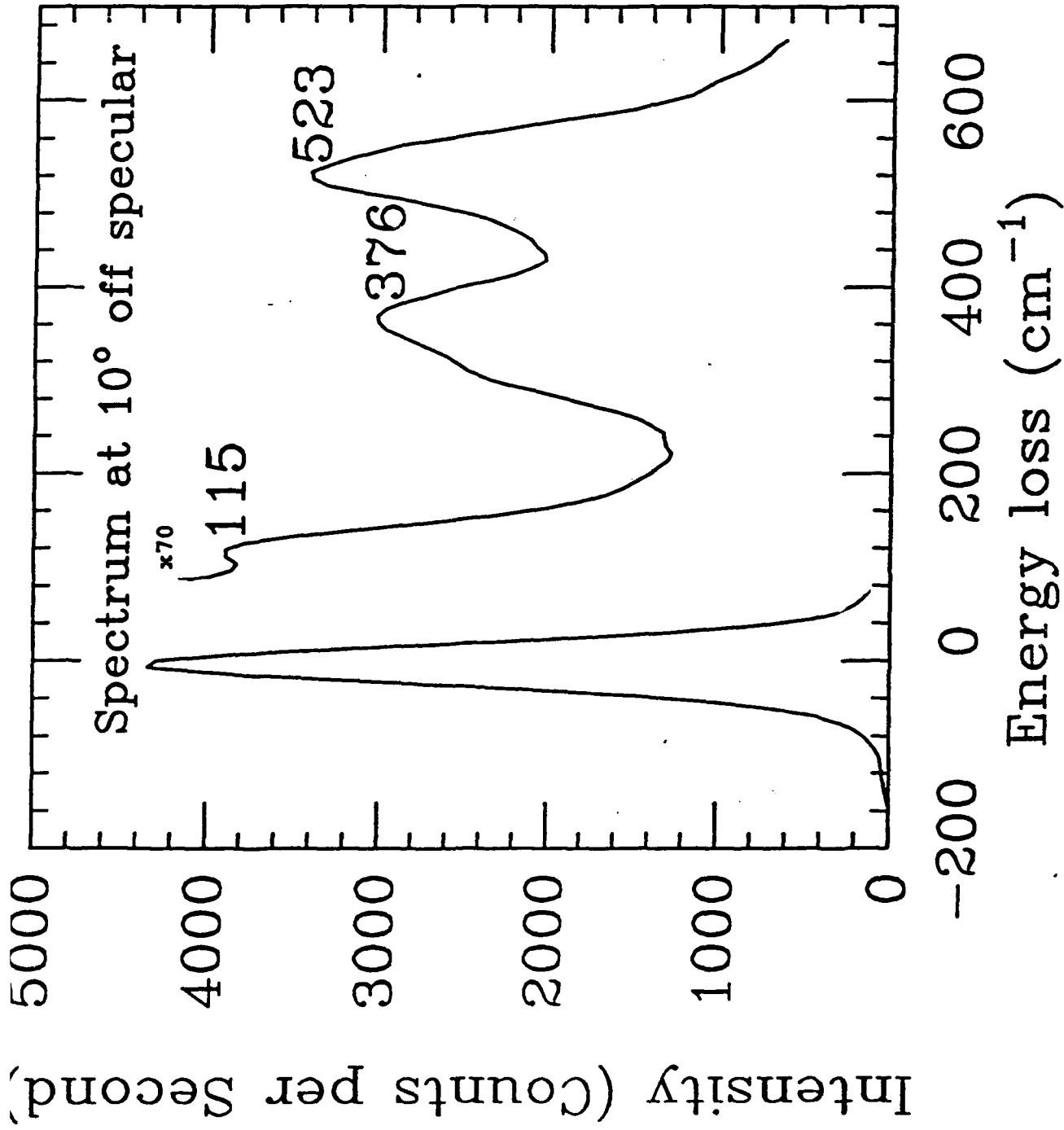
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